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IS 1448-80 (1973): Methods of test for petroleum and its products, Part 80: Determination of trace elements in Petroleum products -- Lead [PCD 1: Methods of Measurement and Test for Petroleum, Petroleum Products and Lubricants]

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Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS :

[P : 80]

DETERMINATION OF TRACE ELEMENTS IN PETROLEUM PRODUCTS — LEAD

(First Reprint DECEMBER 1998)

UDC 665·6/·7 : 543·064 : 546·815

Adapted from Institute of Petroleum Method No. IP 224/68 *T.*

1. SCOPE

1.1 The method is suitable for the determination of trace amounts of lead in a variety of petroleum products. Lead contents ranging from parts per billion (ppb, 1 in 10^9) to parts per million (ppm, 1 in 10^6) can be determined.

2. OUTLINE OF THE METHOD

2.1 A known volume of sample is shaken with aqueous iodine monochloride solution when any lead compound present passes into the aqueous phase. Organolead compounds are then converted to the inorganic form by boiling the solution, and the excess reagent destroyed with sodium sulphite. After addition of buffer solution, the lead is extracted as dithizonate and determined colorimetrically.

3. APPARATUS

3.1 Separating Funnels — glass stoppered and of sufficient capacity to accommodate the chosen sample size (for example, not more than 4 times the volume of sample plus reagents).

NOTE 1 — All glassware shall be of borosilicate.

NOTE 2 — Stopcock grease is often a source of contamination. Lubricate separating funnel taps with a polytetrafluoroethylene (PTFE) aerosol spray or employ PTFE taps.

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MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

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3.2 Beakers — 125 and 250 ml, conical.

3.3 Spectrophotometer — capable of measuring light absorption at a wavelength of 520 nm.

3.4 Optional Apparatus — the 'All purpose' Lovibond comparator, together with 5-mm or 20-mm optical cells, and the Lovibond ref. 5/17 disk.

4. REAGENTS

4.0 Quality of the Reagents — Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070 - 1960*) shall be used in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4.1 Dithizone Solution — 60 mg/l. Dissolve 60 mg of dithizone in 200 ml of chloroform and then add 800 ml of carbon tetrachloride and mix thoroughly. Store the solution in a refrigerator or a cool and dark place.

NOTE — Eastman Kodak dithizone is recommended for this purpose.

4.2 Potassium Iodide Solution — 25 percent (*m*/*v*). Dissolve 250 g of potassium iodide in 500 ml of distilled water. Make the solution slightly alkaline by adding 2 or 3 drops of concentrated ammonia solution. Transfer the solution to a separating funnel and 'delead' it by shaking with successive 20-ml portions of the dithizone solution. Repeat this deleading procedure, separating the chloroform layer each time, until the initial green colour of the dithizone remains unchanged. Add sufficient dilute nitric acid to make the solution just acidic to litmus paper and then shake with 50 ml of chloroform to remove any dissolved dithizone. Allow to stand until the aqueous phase is clear and separate off the chloroform layer. Repeat the washing procedure until the chloroform is colourless. Run the deleaded potassium iodide solution into a 1-litre volumetric flask and make up to the mark with distilled water.

4.3 Iodine Monochloride Reagent — 1·0 M. Mix 445 ml of deleaded potassium iodide solution (*see* **4.2**) with 445 ml of hydrochloric acid (relative density 1·18). Add 75·0 g of potassium iodate slowly with cooling, and stirring until all free iodine initially formed has redissolved to give a clear orange-red solution. Cool to room temperature and dilute to 1 litre with distilled water. Store in a Pyrex, glass-stoppered bottle.

NOTE — Iodine monochloride reacts with rubber, so rubber bungs shall never be used to stopper vessels containing the solution.

CAUTION : Iodine monochloride will react with ammonium ions under certain conditions to yield nitrogen tri-iodide. Care must be taken, therefore, that this reagent does not come into contact with ammonia or ammonia salts.

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*Specification for water, distilled quality (*revised*).

4.4 *o*-Cresol Red Indicator Solution — aqueous, 0·1 percent (*m/v*).

4.5 Ammonia Solution — concentrated, relative density 0·880, 'low in lead' reagent.

4.6 Sulphite-Cyanide Solution — Dissolve 250 g of hydrated sodium sulphite ($Na_2SO_3.7H_2O$) in about 900 ml of distilled water. Delead the solution by extraction with successive portions of dithizone solution until the green colour of the dithizone extract is unchanged. Wash the solution with chloroform to remove the bulk of dissolved dithizone and allow to stand until the aqueous phase is clear. Separate off the chloroform phase and run the aqueous layer into a 1-litre volumetric flask. Add 12·5 g of potassium cyanide (CAUTION), and shake until dissolved. Make up the volume of the aqueous solution to 1 litre with distilled water.

CAUTION : Handle potassium cyanide with rubber gloves in vented hood and wash hands frequently. Drain excess and waste solutions in a hooded sink not used for the disposal of acids and flush with water.

4.7 Sodium Sulphite Solution — saturated. Dissolve approximately 100 g of hydrated sodium sulphite ($Na_2SO_3.7H_2O$) in 100 ml of distilled water and delead as in **4.2**.

4.8 Ammonium Citrate Solution — 46 percent (*m/v*). Weigh 200 g of citric acid monohydrate into a beaker, add about 50 ml of distilled water and place the beaker in an ice/water cooling bath. Add sufficient *o*-cresol red indicator solution to give a definite colour and then add ammonia (relative density 0·88) slowly with stirring until the alkaline (red) colour of the indicator is just developed. Dilute the solution to 500 ml with distilled water and delead the solution by extraction with successive portions of dithizone solution until the green colour of the dithizone extract remains unchanged Wash the solution with chloroform to remove any dissolved dithizone. Allow to stand until the aqueous phase is clear and separate off the chloroform phase. If necessary, filter the solution through a glass wool plug to remove any particulate matter.

4.9 Buffer Solution — Mix 400 ml of sulphite/cyanide solution, 20 ml of ammonium citrate solution (*see* **4.8**), 350 ml of the ammonia solution (relative density 0·88), and dilute to 1 litre with distilled water.

4.10 Stock Lead Nitrate Solution — Dry some lead nitrate in an oven at 105°C for 1 hour and cool to room temperature in a desiccator. Weigh out accurately 1·599 g of the dried lead nitrate and dissolve it in 300 ml of distilled water containing 10 ml of concentrated nitric acid (relative density 1·42). Dilute to 1 litre. One millilitre of this solution contains 1 000 μg of lead.

4.10.1 *Standard Lead Nitrate Solution 1* — Dilute 10 ml of the stock solution to 1 litre with distilled water. One millilitre of this solution contains 10 μg of lead. This solution is used for preparing a 0 to 50 µg of lead calibration curve. It is unstable and shall be freshly prepared for each calibration.

4.10.2 *Standard Lead Nitrate Solution 2* — Dilute 100 ml of the standard lead nitrate solution 1 to 500 ml with distilled water. One millilitre of this solution contains 2 µg of lead. This solution is used for preparing a 0 to 16 µg of lead calibration curve. It is unstable and shall be freshly prepared for each calibration.

5. PREPARATION OF APPARATUS

5.1 All glassware used in the procedure shall be washed with nitric acid and then with distilled water immediately before use. New apparatus should be soaked in chromic acid for 24 hours prior to the above treatment.

6. CALIBRATION

6.1 Calibration curves shall be drawn prior to the spectrophotometric determination. The absorption of the dithizonate solution is measured at a wavelength of 520 nm.

If a Lovibond comparator and ref. 5/17 disk is used, no calibration is required.

Preferably prepare the calibration curve in one batch using the appropriate number of 250-ml conical beakers and separation funnels.

6.2 Add 10 ± 0·2 ml of iodine monochloride solution to each beaker followed by:

a) *For 0 to 50 µg of Lead* — Leaving one beaker as the reagent blank, add to successive beakers 1·0, 2·0, 3·0, 4·0 and 5·0 ml of standard lead nitrate solution 1. (This corresponds to 10, 20, 30, 40 and 50 µg of lead.)

b) *For 0 to 16 µg of Lead* — Leaving one beaker as the reagent blank add to successive beakers 2·0, 4·0, 6·0 and 8·0 ml of standard lead nitrate solution 2. (This corresponds to 4, 8, 12 and 16 µg of lead.)

6.3 To all the beakers add 50 ml of distilled water. While stirring, add saturated sodium sulphite solution dropwise until the precipitated iodine redissolves and the solution is decolorized. Make just alkaline to litmus with concentrated ammonia. Transfer the solution quantitatively to successive 250-ml separating funnels and allow to cool. Add 50 ml of buffer solution to each separating funnel and shake well.

Pipette accurately into each funnel 10 ml of dithizone solution. Shake each funnel and contents for 30 seconds, and then allow these to stand until the two phases have separated and the lower layer has cleared.

Run each lower layer into an appropriate size of optical cell and measure the absorption of the solution at 520 nm.

6.4 Plot calibration curves relating the optical density readings to the actual micrograms of lead added.

7. PROCEDURE

7.1 Analysis of Sample

7.1.1 For unknown concentrations of lead a preliminary test using 5 ml of sample is recommended to establish the approximate lead content. If necessary, a more precise determination can then be carried out using the sample size given in Table 1.

TABLE 1 RECOMMENDED SAMPLE SIZES

Sl No.	Volume of Sample	Lead Expected Range Extended Upwards by Increasing Volume of Dithizone	Size of Comparator Optical Cell
(1)	(2)	(3)	(4)
	ml	ppm	mm
i)	2	5-25	5
ii)	5	2-10	5
iii)	10	1-5	5
iv)	25	0·4-2·0	5
v)	50	0·2-1·0	5
vi)	100	0·1-0·5	5
vii)	250	0·05-0·20	5
		0·02-0·06	20
viii)	500	0·005-0·03	20
ix)	1 000	0·003-0·015	20

7.1.2 Into an appropriate size of separating funnel, add 10 ± 0·2 ml of the iodine monochloride solution. (A reagent blank shall also be carried through these steps but omitting the sample.) Adjust the temperature of the sample at 13 to 18°C and accurately measure the appropriate volume of sample into the separating funnel. (For example volumes below 25 ml, add 25 ml of petroleum ether, kerosine or suitable low olefin hydrocarbon. The requisite quantity of diluent should be included in the blank determination to account for any trace of lead introduced with the diluent.) Stopper the funnel and shake for 3 minutes to thoroughly mix the contents. Allow to stand until the two layers have separated. (With high olefin content basestocks it may be necessary to filter the mixture through a plug of lead-free glass wool into another separating funnel in order to observe the separation. The glass wool removes iodine addition products which collect at the interface.) Run the lower aqueous extract into a 125-ml conical beaker. (If the lower aqueous solution is pale yellow or colourless repeat the extraction with 10 ml portions of iodine monochloride reagent until the colour of the reagent remains relatively unchanged.) Wash the petroleum layer with three 10-ml washes of distilled water adding all the washings to the beaker.

7.1.3 Place the beaker and contents on a hot-plate and boil for 1 minute to complete the decomposition of lead alkyls. Remove the beaker from the hot-plate and cool to room temperature.

7.1.4 Add saturated sodium sulphite solution dropwise until the precipitated iodine redissolves and the solution is decolorized. Make just alkaline to litmus paper with ammonia. Transfer the solution quantitatively to a 250-ml separating funnel and allow to cool. Add 50 ml of buffer solution, shake well, and by means of a pipette, add 10 ml of the dithizone solution. Shake for 30 seconds, and allow to stand until the two layers have separated. Note the colour of the aqueous layer. If sufficient dithizone has been added this will have the well-defined orange colour. If it is colourless or pale-yellow, add the dithizone solution in 10-ml portions until the colour of the aqueous layer is a definite orange after further shaking for 30 seconds. Note the volume of dithizone solution added and use the same volume for the blank.

7.1.5 When the lower organic layer has cleared, run it into the appropriate optical cell and proceed as follows according to the type of equipment used:

a) *Spectrophotometer* — Measure the absorption of the solution at 520 nm. Read off the micrograms of lead in the sample from the appropriate calibration curve.

b) *Comparator* — Compare the sample solution with the calibrated disk, using the dithizone solution from the blank in the comparison cell.

8. CALCULATION AND REPORTING

8.1 Calculate the lead content of the sample from:

$$\text{Lead content of sample in mg/litre or ppm } (m/v) = \frac{\text{micrograms of lead in sample}}{\text{volume of sample taken in ml}}$$

8.2 Report the results to two significant figures as lead content mg/litre or ppm (m/v).

NOTE — Factors established for the Lovibond ref. 5/17 disk under these conditions are:

$$\text{Micrograms of lead in sample using 5-mm cell} = \frac{\text{disk reading} \times 1\,000 \times \text{dithizone used in ml}}{2{\cdot}8}$$

$$\text{Micrograms of lead in sample using 20-mm cell} = \frac{\text{disk reading} \times 1\,000 \times \text{dithizone used in ml}}{10{\cdot}6}$$

9. PRECISION

9.1 Results of duplicate tests shall not differ by more than the following amounts:

a) *Spectrophotometric Method*

Repeatability	*Reproducibility*
$0{\cdot}154\,0 \times X^{0{\cdot}838\,3}$	$0{\cdot}452\,1 \times X^{0{\cdot}838\,3}$

where

X = mean result.

In tabular form these precision estimates give the following typical values:

Mean result	0·1	0·5	1·0	5·0	10·0	20·0
Repeatability	0·022	0·08	0·15	0·59	1·0	1·9
Reproducibility	0·066	0·25	0·45	1·74	3·1	5·5

b) *Comparator Method*

Repeatability	*Reproducibility*
$0{\cdot}356\,0 \times X^{0{\cdot}519\,9}$	$0{\cdot}767\,5 \times X^{0{\cdot}784\,3}$

where

X = mean result.

In tabular form these precision estimates give the following typical values:

Mean result	0·1	0·5	1·0	5·0	10·0	20·0
Repeatability	0·108	0·24	0·35	0·82	1·1	1·6
Reproducibility	0·126	0·44	0·76	2·7	4·6	8·0